

УДК 621.715.539.376

PACS 61.05.cm, 61.46.Hk, 62.20.Qp.68.37.Hk, 81.15.-z

Effects of Al doping on the structural and optical properties of ZnO thin films deposited by (CVD)

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In this paper the methods of receiving thin films from transparent conductive oxide (TCO) ZnO pure and doped for Various concentration of aluminum Al(1,5,10%) using technique chemical vapor deposition (CV) where presented. Obtained high purity pattern, and the deposited thin film can be injected by any item, accordingly to the required option. The structural characteristics have been studied by X-ray diffractometer spectrometer. The results from the X-ray diffraction show that all the pure thin films had a polycrystalline structure of the hexagonal Wurtzite Type. The diagnostics show preferred peaks for the growth of the crystal grains in the directions (002). The optical measurements have shown that the absorption edge is shifted towards the shortwave lengths which mean that the energy gap increases with the increase of Aluminum in ZnO. Also we studied the electrical properties for ZnO:Al. The electric conductivity of ZnO films doped with aluminum increases with the increase in temperature.

Keywords: Thin film, chemical vaporous deposition, ZnO:Al, spray pyrolysis.

В этой статье приведены методики получения тонких пленок из прозрачных проводящих оксидов (TCO) чистых и легированных пленок ZnO для различных концентраций алюминия Al (1,5,10%), используя метод химического осаждения паров (CVD)ю Полученны образцы высокой чистоты и нанесенные тонкие пленки могут быть введены для любого материала, соответственно необходимому варианту. Структурные характеристики изучались методом рентгеновской дифракции, спектрометрию Результаты рентгеновской дифракции показывают, что все чистые тонкие пленки были поликристаллическими, имели гексагональную структуру типа вюрцита. Диагностика показывает предпочтительные пики роста кристаллических зерен в направлениях (002). Оптические измерения показали, что край поглощения смещается в сторону коротковолновой длины, что означает, что ширина запрещенной зоны возрастает с увеличением алюминия в ZnO. Были изучены электрические свойства ZnO: Al. Электропроводимость пленок ZnO, легированных алюминием увеличивается с повышением температуры.

Ключевые слова: тонкие пленки, химическое газовое осаждение, ZnO: Al, пиролиз водных растворов.

У цій статті наведені методики отримання тонких плівок з прозорих провідних оксидів (TCO) тонких плівок ZnO, чистих і легованих для різних концентрацій алюмінію Al (1,5,10%), використовуючи метод хімічного осадження парів (CVD). Отримані зразки високої чистоти і нанесені тонкі плівки можуть бути впроваджені з будь-якого матеріалу, відповідно неогбхідному варіанту. Структурні характеристики вивчалися методом рентгенівської дифракції, спектрометрії. Результати показують, що за рентгенівської дифракції, всі тонкі плівки були полікристалічними за гексагональною структурою. Діагностика показує кращі піки росту кристалічних зерен у напрямку (002). Оптичні вимірювання показали, що край поглинання зміщується в бік короткохвильової довжини, що означає те, що ширина забороненої зони зростає із збільшенням алюмінію в ZnO. Були вивчені електричні властивості ZnO: Al. Електропровідність плівок ZnO, легованих алюмінієм збільшується з підвищенням температури.

Ключові слова: тонкі плівки, хімічне пароподібне осадження, ZnO: Al, пиролиз водних розчинів.

Introduction

Zinc Oxide (ZnO) film with a large band gap of about 3.3 eV is one of the most potential materials for being used as a TCO because of its good electrical and optical properties, abundance in nature, absence of toxicity[1,2] and the ability to deposit these films at relatively low temperatures[3]. The oxygen vacancies and/or zinc

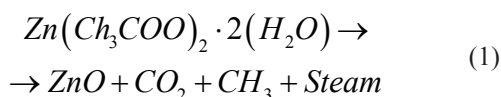
interstitials correspond to the n-type conductivity of the ZnO films. The resistivity of these films can be further lowered by doping them with group III elements like B, Al, Ga or In. Among all these elements, Al is considered to be a good doping for opto-electronic applications like solar cells due to the high transmittance that Al-doped ZnO films exhibit. ZnO has a hexagonal wurtzite structure with the divalent cation (Zinc) in tetrahedral coordination

with oxygen, and each oxygen in tetrahedral coordination with four divalent cations (zinc) [4]. Several deposition techniques have been used to grow doped ZnO thin films including chemical vapor deposition [3] magnetron sputtering [4], spray pyrolysis [2] pulsed laser deposition [5], chemical beam deposition [2]. The process of deposition and producing homogeneous films using (CVD) method is not a simple process but requires a number of tests including the selection of the precursor material, the temperature of substrates, the evaporation temperature and the flow rate of the carrier gasses in addition to the location of the sample in the deposition chamber. All these factors have a direct effect on the type of the required prepared film that and on its physical properties. The characteristics of the chemical vaporization deposition as follows:

- Obtaining at the high purity pattern,
- The formed thin film will be coherent with regular thickness,
- The deposited thin film can be injected by any item, accordingly to the required option,
- The properties of thin film can be controlled through the control of the effective factors of the deposition,
- The system is characterized by cheapest cost, and easily used with availability of raw-material.

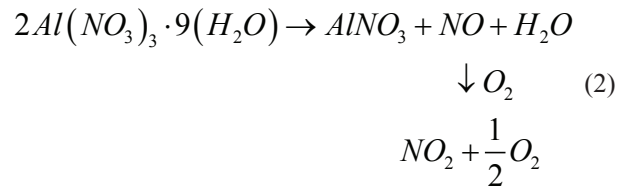
Experimental procedure

In order to prepare pure ZnO films using chemical vapor deposition (CVD) techniques on glass substrates the deposition material used was pure zinc acetate hydrous $Zn(CH_3COO)_2 \cdot 2H_2O$ with 98% purity. After preparing the substrates, they were placed and adjusted in the deposition unit while the temperature degrees were adjusted to (500C°) in order to ensure optimum film properties. The pressurized air flow was also adjusted to the best flow rate which was found to be 2 L/min to produce the best samples as, the rate of airflow is related to the uniformity of the deposited film and it must be adjusted to prevent the formation of colored strips on the glass substrates that can interfere with visional and microscopic inspection. Various temperature degrees were tested when heating the deposition material and it was found that the temperature of (340 C° -350C°) is the appropriate temperature degree range. Deposition time was kept constant at (20 minutes) for the both the pure and doped samples in order to determine the combination of optimal duration with temperature degree that produces the best results of zinc oxide deposition and the samples were left afterwards to cool. The following equations show how ZnO is produced.



The choice of doping material was to use aluminum nitrate hydrous with a purity of (98.5%). After using this

compound, aluminum doped ZnO films were successfully produced with good homogeneity. The various weight percentages of this used material were between (1 - 10%) that were added to the weight percentages of zinc acetate.



The structure of thin films and targets was analyzed using an X-ray diffraction, the absorbance (A) spectra were measured for all pure ZnO films and ZnO films doped with aluminum and prepared on glass substrates and in various deposition conditions as a function of wavelength within the (300-1000nm) range using UV-visible range spectrophotometer mode Ce 1021 at room temperature. The optical parameters of ZnO films and ZnO films doped with aluminum included. The investigated effect of deposition temperature and doping percentages on the transmission spectra and absorbance spectra with the UV-Visible region.

Calculating absorption coefficient and the effect of deposition temperature and doping percentages on this coefficient. The photon energy was calculated as a function of the wavelength from

$$hv(eV) = \frac{1.24}{\lambda(um)} \quad (3)$$

The optical energy gap was calculated from the intersect of $(\alpha h\nu)^2$ with the photon energy axis (hν). The absorption coefficient (α) is a measure of the percentage of loss of light in a beam passing through a specified thickness. The electric measurements in the study included the measurement of D.C conductivity (σ D.C), in order to perform the D.C conductivity measurement at both (low and high temperatures) a system called cryostat was utilized.

Results and discussion

In order to study the effect of aluminum concentration on the microstructure properties of Al doped ZnO thin films, samples with different value of doping concentration (0, 1, 5, and 10%) were used. The X-ray diffraction of four films is shown in Fig. (1, a, b, c, d) It indicated that the film is a polycrystalline structure with hexagonal structure, the XRD profile show three pronounced diffraction peaks at $2\theta = 31.76, 34.47$ and 36.24 position. These peaks corresponds to the (1 0 0), (0 0 2), and (1 0 1) planes of ZnO, for all the samples that were prepared on glass at a temperature of 500 C° and at a doping percentage of (0, 1, 5, and 10%). From the diffraction profile we see that the (002) peak is much stronger than the other peaks. This implies that the ZnO films are strongly c-axis oriented.

The 1% aluminum doped ZnO thin film had the highest (0 0 2) diffraction peak intensity. Moreover, the peak intensities of those films decreased with increased doping concentrations. This indicates that an increase in doping concentration deteriorates the crystalline of films, which may be due to the formation of stresses by the difference in ion size between zinc and doping, and the segregation of dopants in grain boundaries for high doping concentrations. Besides, a slight shift was observed in the peaks in the direction of the lesser angles which may be attributed to the small increase in the bond. These result were confirmed with those obtained from the Joint committee of powder diffraction standards JCPDS for the ZnO

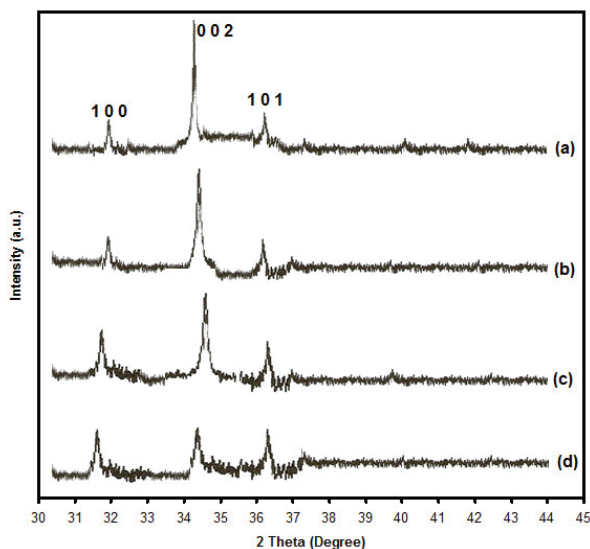


Fig. 1. Show X- Ray diffraction of pure ZnO films and ZnO film doped with Al, a) ZnO pure, b) ZnO doping with Al 1%, c) ZnO doping with Al 5%, d) ZnO doping with Al 10%.

Figures (2) show the absorption spectra as a function of the wavelength of the pure ZnO films and the ZnO films doped with (1,5,10%) aluminum and deposited on substrates heated to (500C⁰). From figure, we can see the transmission decreased with decrease wavelength, and its value large with the visible and infrared spectrum wavelengths and this value decrease approach to the wavelengths of UV, which shows that for these thin films a lot of energy gap to allow access most “visible light. Also be seen from these figures the transmission increases with the increase concentration of doping aluminum. The highest transmission is observed at 500C⁰ and (10%) doping. as, this can be explained that the substrates temperature (500C⁰), causes to improve the crystal structure, that the improvement happened to the transmission of these thin films to increase the concentration of aluminum doping and substrates temperature, due to the existence Al₂O₃ of which had been diagnosed in X-rays diffraction, also we can see two regions are obvious:

The first was the region wave length energy larger than

the energy gap ($E_g > 3eV$) which equals to ($\lambda < 400\text{ nm}$) as during this region, the absorption increase sharply therefore shows that the ZnO: Al can be used as UV protection films.

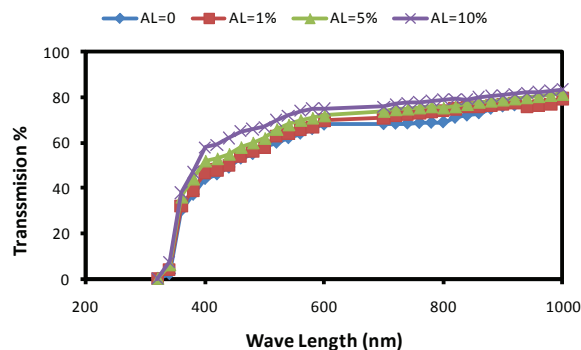


Fig. 2. Transmittance spectra as a function of the wavelength for ZnO:AL samples deposited at (500 C⁰)

The second region lies within the wavelengths range of ($400 < \lambda < 1000\text{nm}$) in which the energy of the incident photon is low and the (ZnO:Al) film is transparent to this range and the absorption is lowest. We can see from the figures (2) that the increase in the percentage of aluminum added to the ZnO leads to the shift in the absorption towards the short wavelengths, a shift that is termed (Burstein-Moss) shift. This type of shift leads to an increase in the optical energy gap, also we can see the decrease of wave length, as its value very high at the wave length which is located with in optical spectrum and infra – red radiation, which indicates that these films have large energy gap to allow most of the visible light to pass as shown in Figure.

Figure (3) shows the relationship between the optical absorption coefficient (α) and the energy of the incident photon ($h\nu$) with temperatures (500C⁰) and doping with Aluminum at a percentage of (1, 5, 10 %). We can see from the figure that the optical absorption coefficient is directly related to the energy of the incident photon as the latter decrease in direct relation to the former.

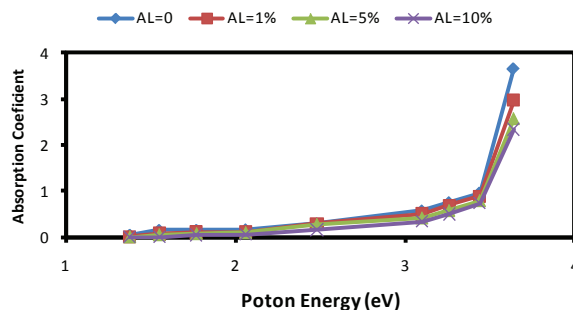


Fig. 3. Optical absorption coefficient (a) of ZnO:AL samples deposited at (500 C⁰)

However, when the films are doped, we find that the optical absorption coefficient decreases with the shift

towards high photonic energies and we find that the pure and doped films have a sharp absorption edge and we find that (α) is larger than (10^4 cm^{-1}) and this value increases with the increase in the photon energy which contributes to the direct traveling of electrons as the high absorption coefficients ($\alpha > 10^4 \text{ cm}^{-1}$) indicates a high probability of direct traveling of electron. The optical energy gap (E_{opt}) is defined as the lowest energy required for the electron to travel from the peak of the coordinate band to the peak of conductivity band and can be calculated directly using the electron traveling formula as follows:

$$\alpha(H\nu) = A(h\nu - E_{opt})^{1/2} \quad (4)$$

And can be rewritten as follows

$$(\alpha H\nu)^2 = A^2(h\nu - E_{opt}) \quad (5)$$

and when $(\alpha h\nu)^2 = 0$, then $E_{opt} = h\nu$.

The relationship between $(\alpha h\nu)^2$ and $(h\nu)$ can be plotted as a curve and the extended part of the curve intersects with the photon energy axis at $(\alpha h\nu)^2 = 0$ and from it we determine the energy gap of direct allowed traveling as shown in figures (4).

Figure (4) shows the energy gaps for pure ZnO and ZnO and doped with a (1,5,10%) aluminum at the temperatures of (500C^0). An obvious increase is observed for the values of the energy gap with the increase in the concentration of aluminum and is in accord with previous studies (4,5) within various preparation techniques. This increase is explained by the proposition that the ZnO:Al films are semiconductors in which the Fermi level lies in the conductive band which means that the levels at the bottom of the conductivity band are occupied by electrons and the shielding of electronic traveling to these levels is termed the Burstein-Moss effect. Also we will discuss the results for the electric conductivity of pure and doped ZnO membranes when the preparation conditions are varied. The most important of the varied conditions is the temperature degree of the substrate material and the percentage of doping as they both have a significant impact on the crystal structure of the ZnO films.

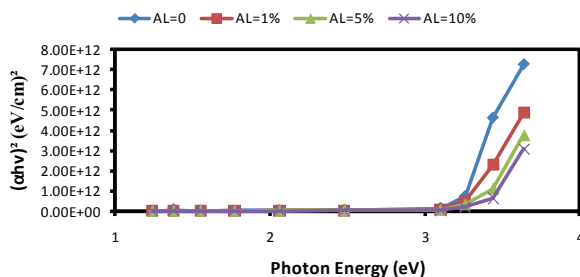


Fig. 4. Measurement of energy band gap (a) of ZnO:Al samples deposited at temperature (500C^0)

Figure (5) shows the change in the electric conductivity of pure ZnO films doped with aluminum at (1, 5, 10%) at substrate temperatures of (400C^0 , 450C^0 , and 500C^0). It is shown that the electric conductivity increases with the increase in the temperature of the substrate and reaches its highest level at a substrate temperature of 500C^0 . The reason attributed to this increase in conductivity with the increase in the temperature of the substrate is the enhanced crystal structure and the increase in the crystal grains which in turn leads to a decrease in the scattering of the charge carriers at the edges of the grains and in turn increases the mobility of the carriers and conductivity. The effect of doping on the electric conductivity was determined at various doping percentages and it was shown in figure (4) that doping had a significant effect on the electric conductivity of ZnO doped with aluminum. At 400C^0 the electric conductivity is low in general when compared with the substrate temperatures of (450C^0 , and 500C^0) and the highest electric conductivity was achieved at approximately 5% doping. The increase in electric conductivity of films doped with an average percentage of aluminum is due to the atoms of triple metals like aluminum that interact with thin film in various ways and the aluminum atoms compensate the Zn locations in the Al_{zn} lattice acting as donors as shown in the following formula:

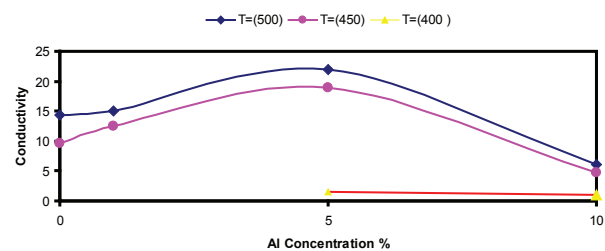
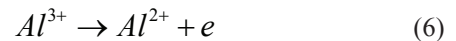


Fig. 5. Shows the change in the electric conductivity of pure ZnO films doped with aluminum at (1, 5, 10%) at substrate temperatures of (400C^0 , 450C^0)

Al^{2+} occupies the locations in the ZnO lattice and (e) the free electrons that participate in electric conductivity. When doping with aluminum at percentages of (1%) and (5%) there was an increase in the electrons with the increase in the values of mobility. The results indicate that the increase in the percentages of doping to (5%) has led to the increase in the donor levels and which in turn led to an increase in the number of atoms that donate electrons and become ions. Doping at 10% led to a decrease in conductivity because of the decrease in the concentration of electrons stemming from the lower mobility, while the decrease in conductivity at high percentages of doping $\leq 5\%$ is due to the decrease in the concentration of charge carriers and mobility because the doped material in this case not only plays the role of donor but also affects the crystal structure and decreases the crystal grains and

therefore increase the scattering process of electrons from the edges of grains .

Conclusion

In this paper we observed a number of observations concerning the films. In some instance the films did not grow over the substrates or they only partly covered them. In other instances we observed that the films were formed as stripes. These cases took place at temperatures less than 400C⁰. While at this temperature and above, we found that the films status was enhanced significantly concerning the rate of growth and homogeneity while the optimal temperature degree in this study was found to be 500 C⁰ as the optical, and electrical properties of the films. And the most important conclusions reached by the study are as follows: Films formed from pure zinc oxide and zinc oxide doped with aluminum show a hexagonal polycrystalline structure with a tendency to grow in the (002) direction An increase in crystal grains appears when doping the films with (1 - 10%) aluminum .The transmission increases with the increase in percentage of doping aluminum. The highest transmission is observed at 500C⁰ and (10%) doping. Zinc oxide films have a high absorption coefficient ($\alpha > 10^4 \text{ cm}^{-1}$) and increases with the doping percentage. The energy gap increases with the doping percentage, the highest value was observed at 500C⁰ and (10%) doping and it is equal to (3.4eV). ZnO films show good electric conductivity at (450and 500C⁰) and was found to be (9.740741 ($\Omega \text{ cm}^{-1}$) and (14.34615($\Omega \text{ cm}^{-1}$).The electric conductivity of The ZnO films doped with aluminum increases with the increase in temperature and the highest was and (14.34615($\Omega \text{ cm}^{-1}$) at 500C⁰ ,and increased with increases with the percentage of doping until the doping percentage of (5%) is reached then starts to decrease with the increase in doping percentages at the temperatures (450 C⁰ and 500C⁰) .

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Table
Results of X- Ray diffraction of pure ZnO films and ZnO film doped with Al.

sample	(2θ)Degree	d (Å)	(h k l)
ZnO	31.7664	2.81463	100
	34.4717	2.59968	002
	36.2439	2.47653	101
ZnO: Al (1 %)	31.7661	2.81466	100
	34.4567	2.5998	002
	36.2425	2.47658	101
ZnO: Al (5 %)	31.7652	2.81473	100
	34.4393	2.60205	002
	36.2417	2.47667	101
ZnO: Al (10 %)	31.7990	2.81182	100
	34.4458	2.60158	002
	36.2650	2.47513	101